J. Environ. Nanotechnol.
Volume 8, No.1(2019) pp. 06 - 12
ISSN (Print): 2279-0748
ISSN (Online): 2319-5541
doi:10.13074/jent.2019.03.191341

Phenolic Compounds Adsorption on Mesoporous *Aluminophosphate* Molecular Sieves from Aqueous Solution

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Received: 08.11.2018 *Accepted: 22.12.2018*

Abstract

The phenolic compounds removal through adsorption was reported on many nature materials and activated carbon, but adsorption on mesoporous AlPO4 was not yet reported. Hence in the present investigation, attempts are made to adsorb phenolic compounds. The formation of mesoporous. AlPO4 is to be confirmed by FT-IR analysis. The mesoporous AlPO4 is used as an adsorbent for the removal of phenolic compounds (phenol & P-cresol). The phenolic compounds adsorption conditions like contact time, pH, initial concentration of the solution, temperature, adsorbent dosage are optimized to obtain maximum adsorption. The Langmuir adsorption isotherm and Freundlich adsorption isotherm are studied on Mesoporous AlPO4 to find out monolayer and multilayer adsorption capacity. The adsorption kinetics of phenolic compounds over mesoporous AlPO4 for calculating from energy, enthalpy and entropy for analyzing thermodynamic parameters of the adsorption.

1. INTRODUCTION

Water pollution control is presently one of the major thrusts areas of scientific research. Years of increased industrial, textile and domestic activities has resulted in the generation of large amount of waste water containing many number of toxic pollutants. Organic pollutants comprise a potential group of chemicals which can be dreadfully hazardous to human health. The most important organic pollutants are phenols and its derivatives (Meena *et al.* 2005; Anjaneyulu, 2005). Chemical pollutants continuously released from various sources raise a number of ecological concerns because their biodegradation is normally very slow and conventional treatments are either ineffective or no environmentally compatible (Hang-Yan Wang, 2009). In recent years, the colour of the effluent discharged into receiving waters has become a serious problems. In order to solve this environmental problem, physical and chemical processes have been investigated , such as coagulation, flocculation, bio sorption, photodecomposition and ultra filtration (Galindo *et al.* 2003; Robinson *et al.* 2001). Among these techniques, adsorption process is a procedure of choice for the removal of organic compounds from waste water (Dabrowshi, 2001).

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Many industries discharge hazardous waste waters provides many problems to human's health including diarrhea, liver damage, anaemia and dark urine (Kumar *et al.* 2007). Especially, Phenols are considered as priority pollutants since they are harmful to organisms at low concerntrations and cause significant taste and odour problems to drinking water (Iffat *et al.* 2004).

2. EXPERIMENTAL

2.1 Materials and methods

The chemicals used in the present work are pure analytical grade and used directly without further purification. Aluminium hydroxide (97%:Merck), phosphoric acid (88%; Nice), the long chain alkyl benzene, (SDBS, 25Wt% in water, Aldrich) are used for the preparation of mesoporous $AlPO_4$. The Phenol and p-Cresol shown in Fig. 1(a) and Fig. 1(b) are used to study the removal or organic pollutant. The properties of phenol and p-cresol are given in Tab le 1. The tetrahedral framework of synthesized mesoporous AlPO4 is confirmed by FT-IR. The fourier transform infrared (FT-IR) measurement of sample is recorded by JASCO-410 FT-IR model spectrophotometer by using KBr pellet technique. A double beam UV/VIS spectrophotometer (Perkin Elmer, Lambada 25) is used to determine the concerntration of samples.

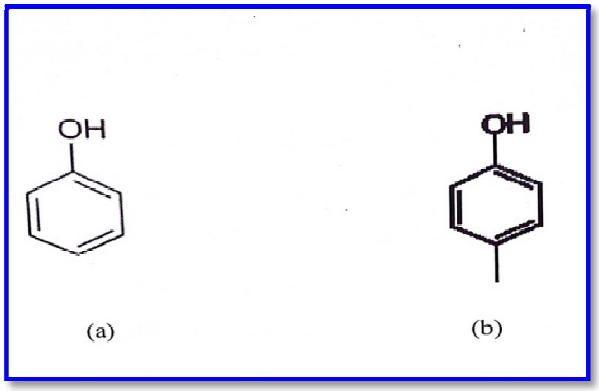

Fig. 1(a) Structure of phenol (b) Structure of p-cresol

2.2 Synthesis of mesoporous $AlPO_4$

In this synthesis, 7.48g of aluminium hydroxide is added to the 17.5g of Sodium dodecyl benzene sulfonate solution with vigorous stirring. Then 9.8g of phosphoric acid solution is added to the mixture. The mixture is stirred for 6hours at room temperature. The final gel with a molar composition, Al_2O_3: P_2O_5: 0.5SDBS: 300H_2O is heated at 150 ^oC with stirring up to the complete precipitation of the aluminophosphate mesoporous molecular sieves. The final product is washed repeatedly with distilled water, filtered and dried at 120 ^oC for 3hours. This as-synthesised sample was calcinated at 600 ^oC for 6hours to remove the template, organic contaminants and activate the active sites of mesoporous aluminophosphate molecularsieves.

2.3 Preparation of stock solution

Stock solution (1000 mg/L) of phenol and p-cresol were prepared by dissolving in double-distilled water. Experimental solutions of the desired concentration are then obtained by successive dilutions with distilled water.

2.4 Adsorption Experiment

The mesoporous $AlPO_4$ is activated by heating in an electric Bunsen at 500 ^oC for 4hours to remove physically adsorbed species present in the pores and surfaces. Then the 0.5g of mesoporous $AlPO_4$ is added with 50ml of phenol and p-cresol solution separately. The solution is agitated (kemi agitator) at 150 rpm. The solution concentration is measured by spectrophotometrically. The maximum adsorbance are found using scanning spectrophotometry at the respective wavelength. The maximum wavelength λ_{max} used are 269 nm and 285 nm for phenol and p-cresol respectively.

To find out the maximum removal of phenol and p-cresol over mesoporous $AlPO_4$, the condition like contact time, pH, dye concentration, temperature and adsorbent dosage are optimized.The effect of contact time is studied up to adsorption equilibrium. The effect of pH is studied in the pH range from 2 to 11. The adsorption of phenol and p-cresol over mesoporous $AlPO_4$ is studied in the concentration range of 10-50mg/L. The temperature effect of adsorption of phenol and p-cresol is studied in the range of 30^oC-70 ^oC. The mesoporous $AlPO_4$ dosage effect is studied in the range of 0.5-2.5g.

The adsorption capacity (mg phenol/g adsorbent) of mesoporous $AlPO_4$ is calculated by using the following equation.

$$q = (C_o - C_e)\ V/W$$

The removal percentage (%) is calculated by using the following equation:

$$\text{Removal in percentage} = (C_o - C_e) \times 100 / C_O$$

Where,

q is the amount of adsorbate adsorbed on mesoporous $AlPO_4$ (mg g^{-1}),

C_O and C_e are the initial and final concerntration of adsorbate in solution (mg L^{-1}) respectively.

V is the volume of solution (L) and W is the adsorbent weight (g).

Amino-antipyrine method for detection of phenol concerntration:

3ml of phenol solution is taken in a 10ml volumetric flask. To this 1ml of ammonia buffer solution, pH=10 and 2ml. of 2%, 4-aminoantipyrine solution and 6ml of 4% potassium ferricyanide solution are added in that order and diluted up to 100ml with distilled water. The solution is checked for complex formation using U.V and Visible spectrophotometer.

3. RESULTS & DISCUSSION

3.1 Characterisation of mesoporous $AlPO_4$

The mesoporous $AlPO_4$ is prepared by following the reported literature. To verify the framework of $AlPO_4$, the FT-IR study has been carried out.

The fourier transformer Infrared of the calcined sample is shown in Fig. 2. The asymmetric stretching of tetrahedral $AlPO_4$ is observed near 1106 cm^{-1} and corresponding symmetric stretching is observed around 674cm^{-1} and bending mode is positioned near 466cm^{-1}. The broad peak at 3423cm^{-1} is due to –OH groups and water molecules present in these molecularsieves. This tetrahedral framework vibration proved the formation of $AlPO_4$ sieves.

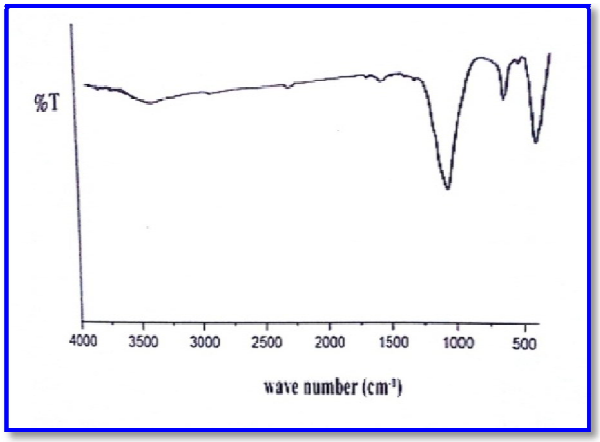

Fig. 2: FT-IR Spectrum of calcined mesoporous $AlPO_4$

3.2 Adsorption studies

The effect of removal of phenol and p-cresol over mesoporous $AlPO_4$ through adsorption at different conditions such as contact time, concerntration, pH, temperature and adsorbent dosage are optimized for maximum adsorption.

3.2.1 Effect of contact time

The effect of contact time has been carried out at room temperature for the adsorption of phenol and p-cresol on mesoporous $AlPO_4$ upto 40 minutes (Fig. 3). Adsorption equilibrium is observed at 30 minutes for both (phenol and p-cresol) and further increased of contact time not much increased the adsorption. Intially large number vacant sites were available for the adsorption, so the adsorption rate is very fast for phenol. The removal of p-cresol from aqueous solution on the mesoporous $AlPO_4$ is far less than the phenol. This shows that different affinities of the phenolic species on the active sites of mesoporous $AlPO_4$.

3.2.2 Effect of pH

The removal of hazardous pollutants phenol and p-cresol is influenced by the pH factor. The effect of pH is studied in the pH range from 2 to 11 (Fig. 4). The pH of the solution are adjusted by using 0.1N NaOH and/or 0.1 N HCl. The adsorption of phenol and p-cresol increased gradually with increase of pH and reach maximum at pH 7. Further increase of pH decreases the adsorption . At pH 7 the adsorption is maximum, below and above 7 adsorption is not favourable. This indicated that at lower the low adsorption at low pH may be due to the protanation of phenolic compounds. Due to this, there is the formation of positive charge on both the adsorbent and adsorbate system. This results the net reduction of phenolic compounds adsorption. With the increase of pH from 5 to 7 the molecular form of phenolic species persists in medium and surface protanation is minimum leading to the enhancement of adsorption.

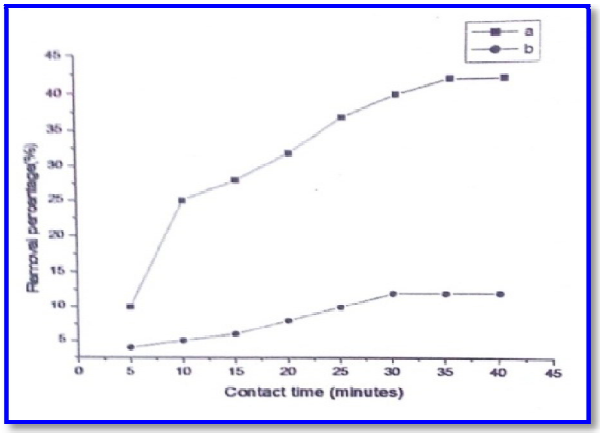

Fig. 3: Effect of contact time for adsorption of a) Phenol and b) p-cresol over mesoporous $AlPO_4$ (Conc.: 10mg/L, Temperature: 30 ^oC, Adsorbent dosage: 0.5g)

3.2.3 Effect of concerntration

The phenol and p-cresol adsorption on mesoporous $AlPO_4$ were studied between the concerntrations range 10mg/L-50mg/L at room temperature is shown in Fig. 5. The adsorption capacity of the mesoporous $AlPO_4$ is found to be maximum at 10mg/L and further increase of concerntration decreased the adsorption of phenol and p-cresol on the adsorbent. The initial concerntration provides an important driving force to overcome all mass transfer resistance of the phenolic compound between the aqueous and solid phase. The phenolic compounds interact with active sites present in the surface and the pores of mesoporous aluminophosphate molecular sieves facilitating phenol and p-cresol adsorption. At higher concerntration, phenolic compounds bound to each other through hydrogen bond and hence the adsorption percentage

decreased. Moreover, at higher concerntration , the surface area and active sites are saturated. Hence, adsorption decreased with increase of concerntration.

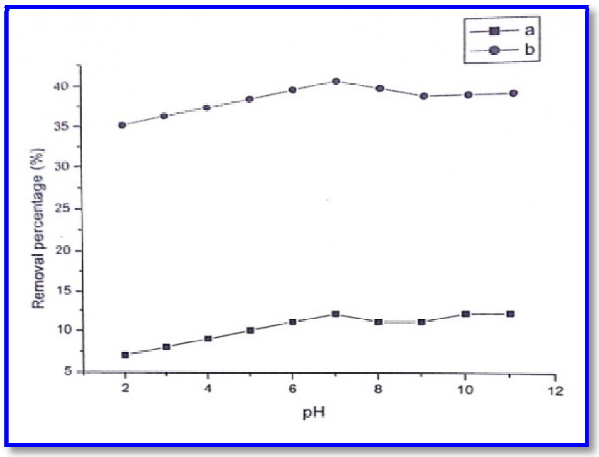

Fig. 4: Effect of pH for adsorption of phenol and p-cresol on mesoporous $AlPO_4$ (Contact time: 30mins, Concerntration: 10mg/L, Temperature: 30°C, Adsorbent dosage: 0.5g)

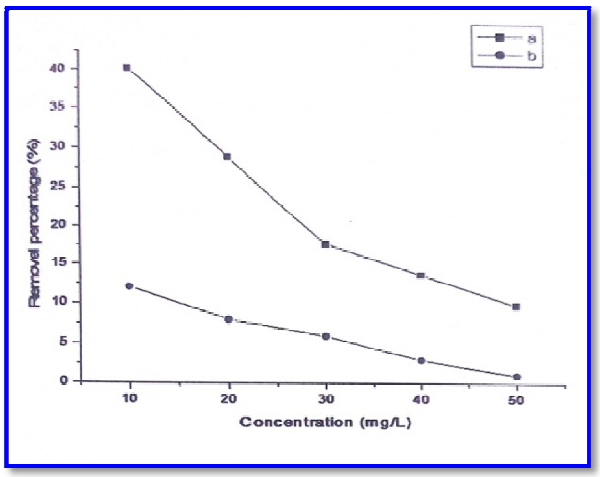

Fig. 5: Effect of concerntration for adsorption of phenol and p-cresol on mesoporous $AlPO_4$ (Contact time: 30mins, Temperature: 30°C, Adsorbent dosage: 0.5g, pH: 7)

3.2.4 Effect of temperature

The effect of temperature for the removal of phenol and p-cresol on mesoporous $AlPO_4$ is studied in the range of 303K to 343K (30°C to 70°C) is shown in Fig. 6. The adsorption increased with increase of temperature from 30 °C to 70 °C indicated that the adsorption process is endothermic. This may due to increase of interaction between adsorbate and adsorbent.

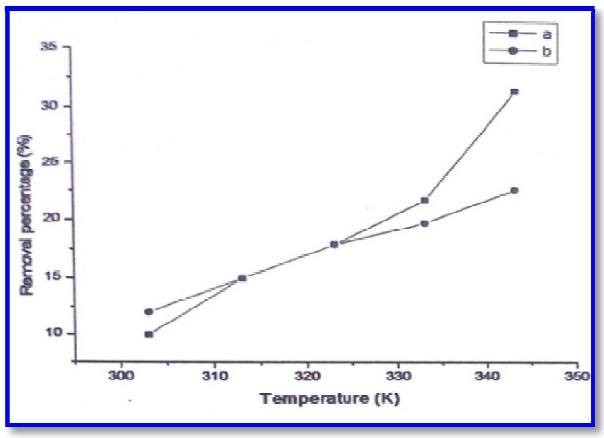

Fig. 6: Effect of temperature for adsorption of phenol and p-cresol on mesoporous $AlPO_4$ (Contact time: 30mins, Concerntration: 500mg/ L, Adsorbent dosage: 0.5g, pH: 7)

3.2.5 Effect of adsorbent dosage

The effect of adsorbent dosage (0.5-2.5g) on adsorption of phenol and p-cresol were studied (Fig. 7). The percentage removal of the phenol and p-cresol were found to be increased with increase of adsorbent dosage. Since the increase of dosage increased the surface area and active sites. Hence, adsorption increased with increase of mesoporous $AlPO_4$.

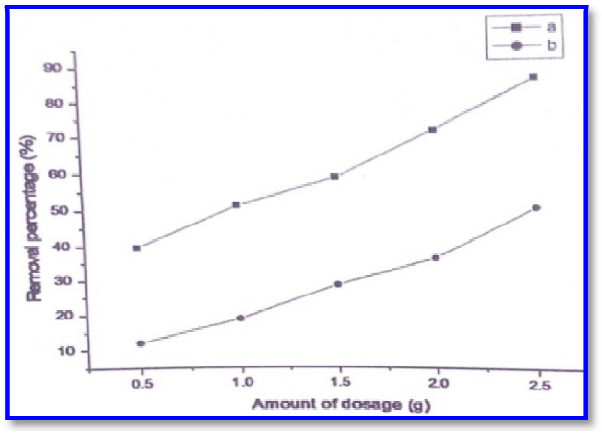

Fig. 7: Effect of Adsorbent dosage for adsorption of phenol and p-cresol on mesoporous $AlPO_4$ (Contact time: 30mins,Concerntration: 500mg/ L,Temperature: 30°C, pH: 7)

4. Adsorption isotherms

The distribution of phenol and p-cresol between the adsorbent and solution is determined by Langmuir and Freundlich isotherms.

4.1 Langmuir adsorption isotherm

Adsorption isotherm data at different concerntrations are measured for the adsorption of phenol and p-cresol and fitted with Langmuir adsorption isotherm equation (Fig. 8). This study has been carried out as a model for understanding the monolayer adsorption of phenol and multilayer adsorption of p-cresol on mesoporous $AlPO_4$.

The Langmuir equation is represented as

$$C_e/Q_e = (1/Q_{max}\, K_L) + (C_e/Q_{max})$$

Where,

Q_e is the equilibrium concerntration of adsorbate on the adsorbent (mg g^{-1})
C_e is the equilibrium concerntration of adsorbate in solution (mg L^{-1})
Qmax is the monolayer capacity of Adsorbent (mg g^{-1})
K_L is the Langmuir adsorption constant

Langmuir constant K_L is a measure of the affinity between adsorbate and adsorbent and 1/ K_L value gives half maximum adsorption. A plot of C_e/Q_e vs C_e is a straight line with slope $1/Q_{max}$ and intercept $1/Q_{max}\, K_L$. The R^2 values for the adsorption of phenol and p-cresol on mesoporous $AlPO_4$ are given in the Table-1.

The correlation coefficient (R^2) values are very close to 1 (R^2 =0.992) for phenol indicated that the adsorption of phenol on mesoporous $AlPO_4$ follows the Langmuir adsorption isotherm. The maximum monolayer adsorption capacity of mesoporous $AlPO_4$ for phenol is 0.5226mg/g. The correlation coefficient (R^2) value is not close to 1 (R^2 = 0.86) for p-cresol and hence the adsorption of p-cresol not follow the Langmuir adsorption isotherm. This may due to the steric effect of methyl group present in the p-cresol. This result clearly indicated that the mesoporous $AlPO_4$ has more affinity with phenol molecule than p-cresol.

4.2 Freundlich adsorption isotherm

The adsorption studies are carried out at various concerntrations for the adsorption of phenol and the adsorption values are applied to the freundlich equation to verify the adsorption isotherms (Table 1). This study has been carried out as a model for understanding the monolayer and multilayer adsorption of phenol and p-cresol.

The Freundlich equation is represented as

$$\ln Q_e = \ln K_F + (1/n)\, \ln C_e$$

where,

K_F is the Freundlich constant and n is the no. of layers.

The plot of $\ln Q_e$ Vs $\ln C_e$ gave a straight line (Fig. 9) with the intercept $\ln K_F$ and the slope 1/n. The correlation coefficient for adsorption of phenol and p-cresol are not close to 1(0.620for phenol and 0.045 for p-cresol). This result revealed that both adsorption processes not follow the freundlich isotherm model.

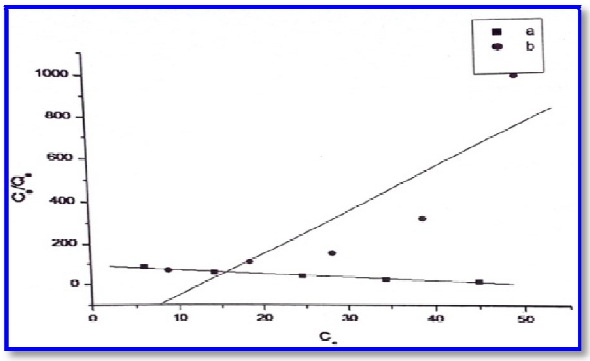

Fig. 8: Linear forms of Langmuir adsorption isotherms plots of phenol and p-cresol on mesoporous $AlPO_4$

Table 1. Langmuir and Freundlich adsorption isotherm parameters

S. No	Langmuir isotherm Parameters	Phenol	p-cresol	Freundlich isotherm Parameters	Phenol	p-cresol
1.	Qmax (mg g)	0.5226	0.0492	1/n	0.1151	0.284
2.	K_L	-7.226	-0.0808	K_F	-.0146	-0.662
3.	R^2	0.99	0.86	R^2	0.620	0.045

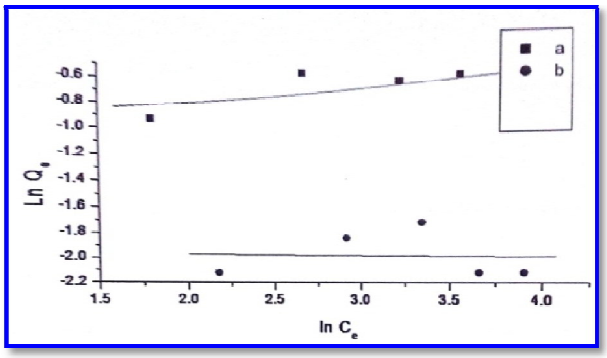

Fig. 9: Linear forms of Freundlich adsorption isotherm plots of phenol and p-cresol on mesoporous $AlPO_4$

5. ADSORPTION KINETICS

The adsorption kinetics of phenol and p-cresol adsorption on mesoporous $AlPO_4$ was studied as a model study for find out the rate constant of the adsorption. The adsorption of phenol was studied at regular time interval at room temperature. The experimental values are introduced in the pseudo second order kinetics equation for calculating the rate constant.

The equation for adsorption kinetics is

$$t/Q_t = 1/kQ^2_e + 1/ Q_e\, t$$

Where, K is the rate constant, Qe and Qt are the amount of adsorbate adsorbed per unit mass of the adsorbent at equilibrium and t is time. The plot of t/ Q_t Vs t gives straight line. Linear plots of the t/Qt Vs t is given in the Fig. 10 for phenol and p-cresol adsorption on mesoporous $AlPO_4$. The linear regression coefficients close to 1 (Table 2) indicated that the adsorption of phenol (R^2=0.96) and p-cresol (R^2=0.907) on mesoporous $AlPO_4$ is fitted with the pseudo-second order kinetics.

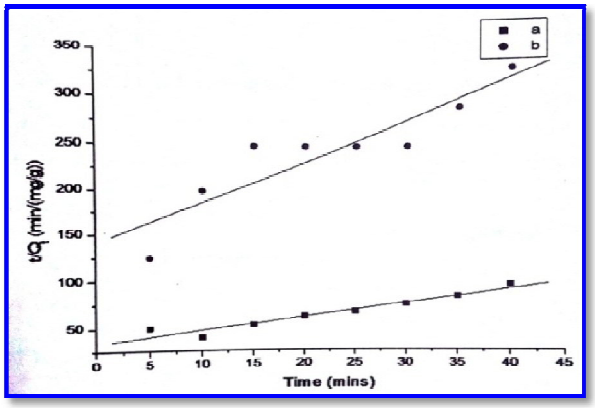

Fig. 10: Linear forms of Pseudo second order kinetics plots of phenol and p-cresol on mesoporous $AlPO_4$

Table 2. Pseudo second order kinetics parameters

S.No	Kinetic Parameters	Phenol	p-Cresol
1.	**K**	0.0611	0.0768
2.	**Q**	0.6972	0.2197
3.	**R**	0.9616	0.9079

6. ADSORPTION THERMODYNAMICS

The thermodynamic parameters, namely free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) have an important role to determine spontaneity and heat change for the adsorption process. The thermodynamic parameters are calculated using the following relations.

$$K_D = q_e/ C_e$$
$$\Delta G = -RT\ln K_D$$
$$\ln K_D = (\Delta S/R) - \Delta H/ RT)$$

From the above equations,

$$\Delta G = \Delta H - T\Delta S$$

Where;

K_D is the distribution coefficient of the adso rbate, q_e and c_e are the equilibrium concerntration of adsorbate on mesoporous $AlPO_4$ (mg g^{-1}) and in the solution (mg L^{-1}), respectively. R is the universal gas constant (8.314 J/mol K) and T is the temperature (K). ΔH^o and ΔS^o parameters can be calculated from the slope and intercept of the plot ln K_D Vs. 1/T, respectively (Fig. 11). ΔG^o was calculated using the equation for different temperatures. Results are summarized in Table 4. ΔG^o values at the temperatures of 303, 313, 323, 323 and 333, 343 K are negative. This indicates that the process is feasible adsorption process and spontaneous.

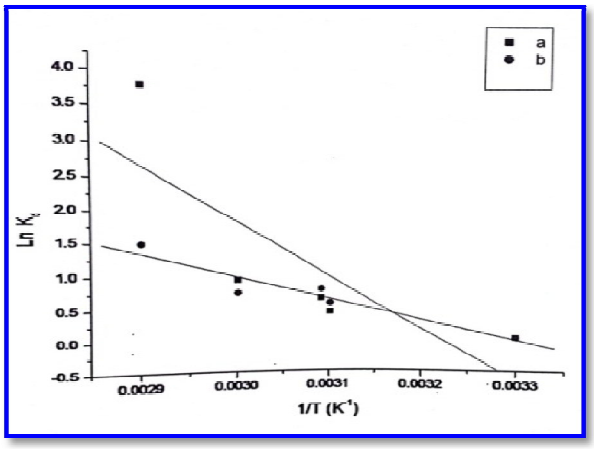

Fig. 11: Linear forms of Adsorption thermodynamic plots of phenol and p-cresol on mesoporous $AlPO_4$.

The enthalpy (ΔH^o) values greater than 40 KJ/mol for phenol (68.64KJ/mol) indicated that the adsorption of phenol over mesoporous $AlPO_4$ is chemisorption and less than 40KJ/mol for p-cresol (27.92KJ/mol) indicated that the adsorption of p-cresol over mesoporous $AlPO_4$ is physisorption. The positive value of enthalpy indicated that the adsorption process is endothermic. Moreover, the positive value of ΔS^o indicated that the degrees of freedom increased at the solid-liquid interface during the adsorption.

Table 3. Thermodynamic parameters for adsorption of phenol and p-cresol

S.No	Thermodynamic Parameters	Phenol	p-cresol
1.	ΔH^o(KJ/mol)	68.64	27.92
2.	ΔS^o (KJ/mol/K)	0.21	0.092
3.	ΔG^o(KJ/mol)		
	T=303 K	-1.677	0.044
	T=313 K	-0.533	-0.876
	T=323 K	-2.743	-1.796
	T=333 K	-1.623	-2.716
	T=343 K	-3.373	-3.631

7. CONCLUSION

Mesoporous aluminophosphate molecular sieve is synthesized successfully. It is suitable for removal of phenol and p-cresol from the aqueous solution. The adsorption equilibrium attained at 30 minutes. It is observed that monolayer adsorption capacity is 0.5226mg/g for phenol. The adsorption isotherm results showed that the adsorption of phenol on mesoporous aluminophosphate molecular sieves follows the Langmuir adsorption isotherm. Adsorption of phenol is not followed the freundlich adsorption isotherm. P-cresol is not followed both adsorption isotherms due to the presence of methyl group. The methyl group inhibits the mono/ multi layer formation. The thermodynamic studies showed that the adsorption process is spontaneous and endothermic. This study concluded that the mesoporous $AlPO_4$ is suitable adsorbent for the removal of phenol.

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